LYOTROPIC LIQUID CRYSTAL – BUTYL RUBBER BLENDED NANOMATERIALS

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Introduction

Uses of Butyl Rubber (BR) as barrier material fabric

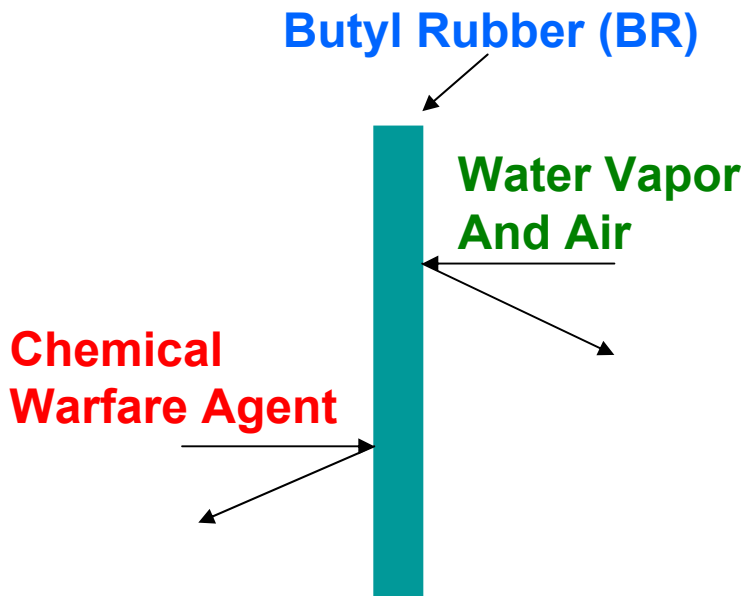
Advantages:

- Low permeability toward gases, organic solvents, water, and reactive chemicals
- Excellent chemical resistance

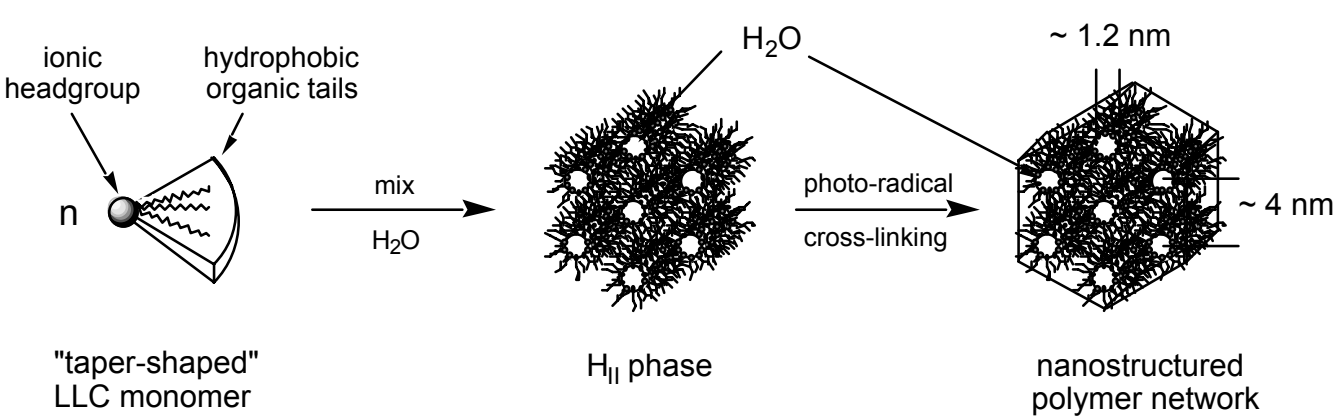
Disadvantages:

- Lack of permeability of air and water vapor

⇨ Development of fatigue and heat stress in wearer



Our Approach



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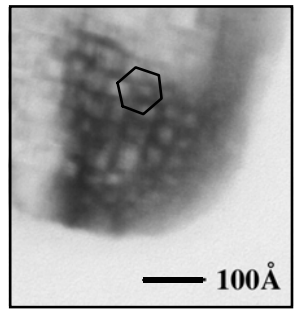
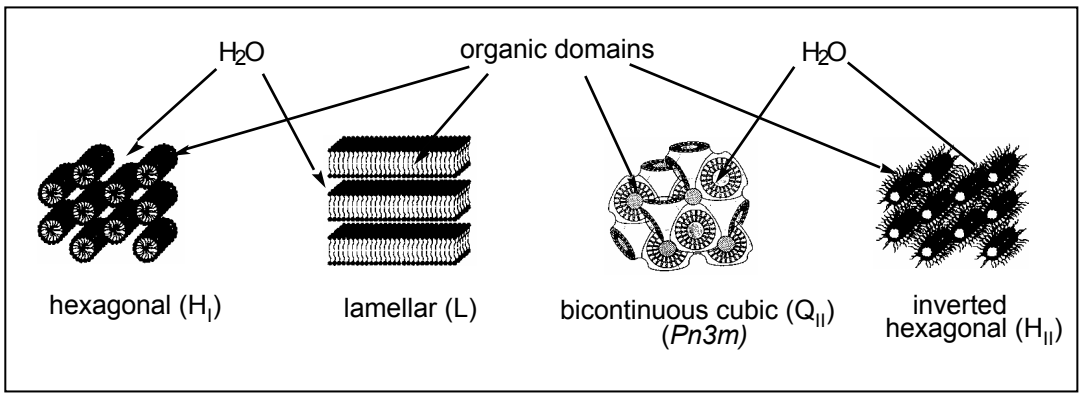
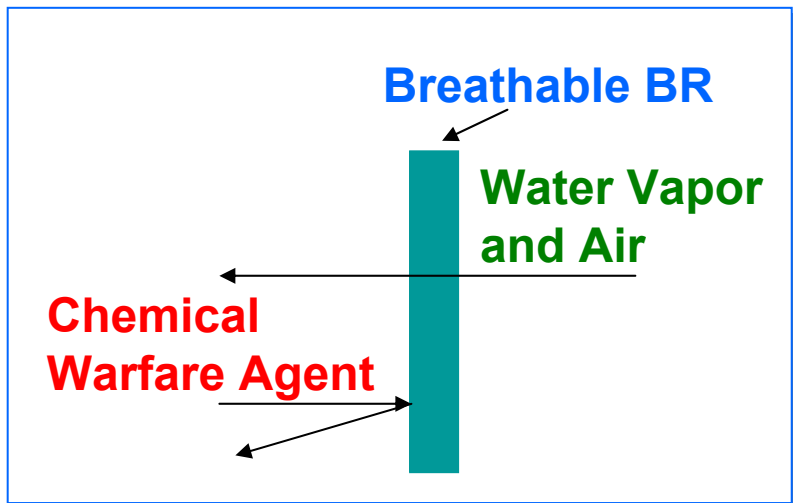


- **Blend BR with lyotropic liquid crystals (LLCs) that form inverted hexagonal (H_{II}) phase**

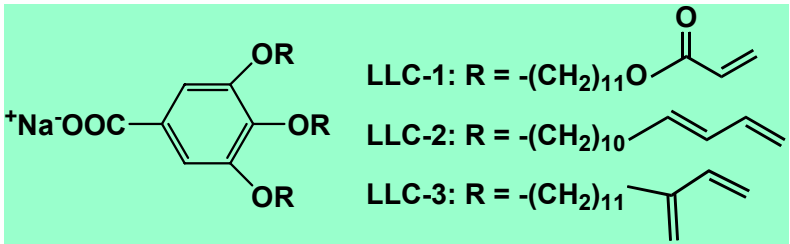
⇒ **Nanoporous Breathable LLC-BR Composite**

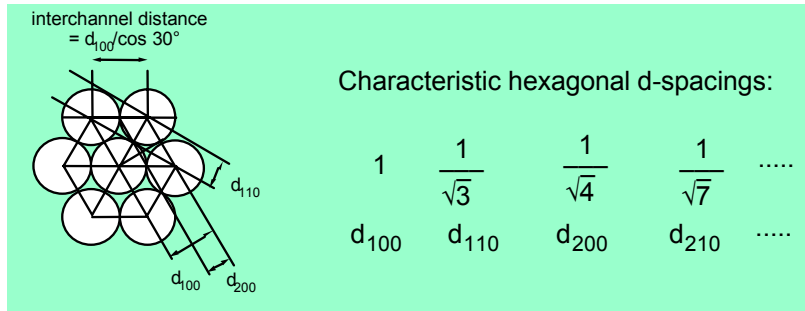


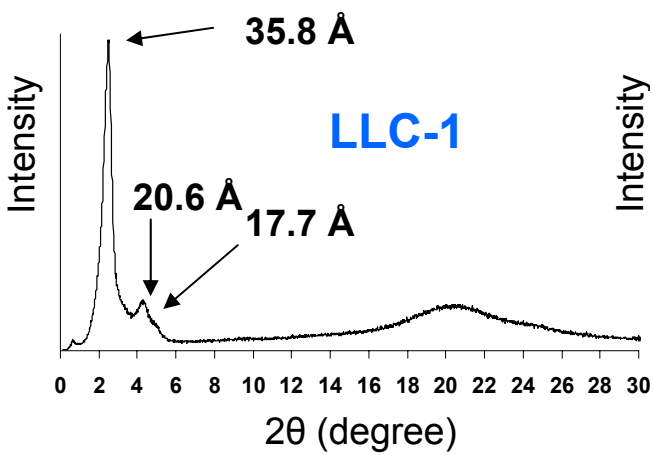
LLC assemblies

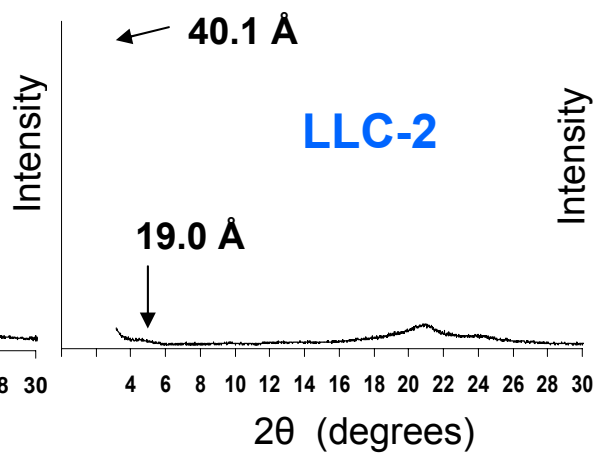


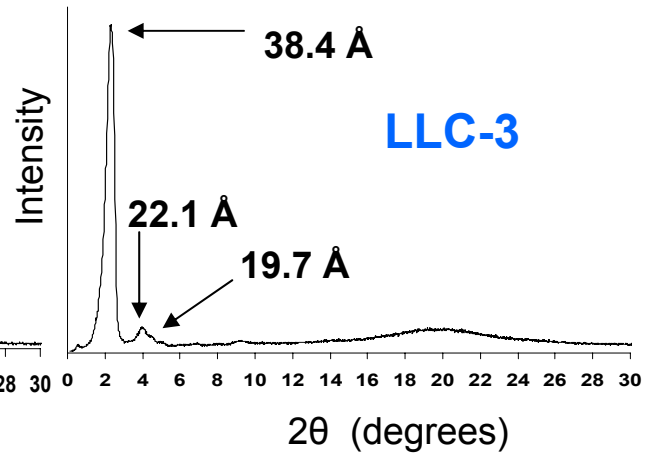
Structure of LLCs and X-ray Diffraction Characterization











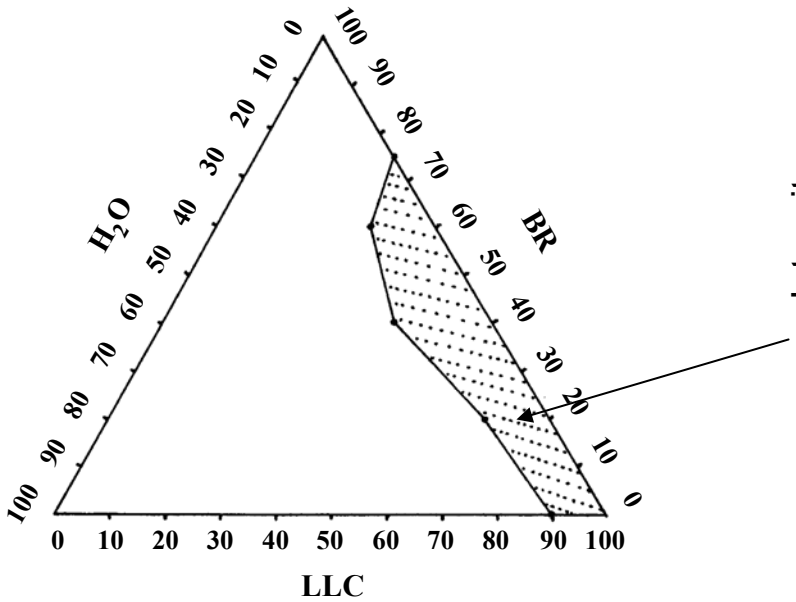
- **All three LLCs form H_{II} phase.**

Smith, R. C.; Fischer, W. M.; Gin, D. L. *J. Am. Chem. Soc.* 1997, *119*, 4092.
Hoag, B. P.; Gin, D. L. *Macromolecules* 2000, *33*, 8549.

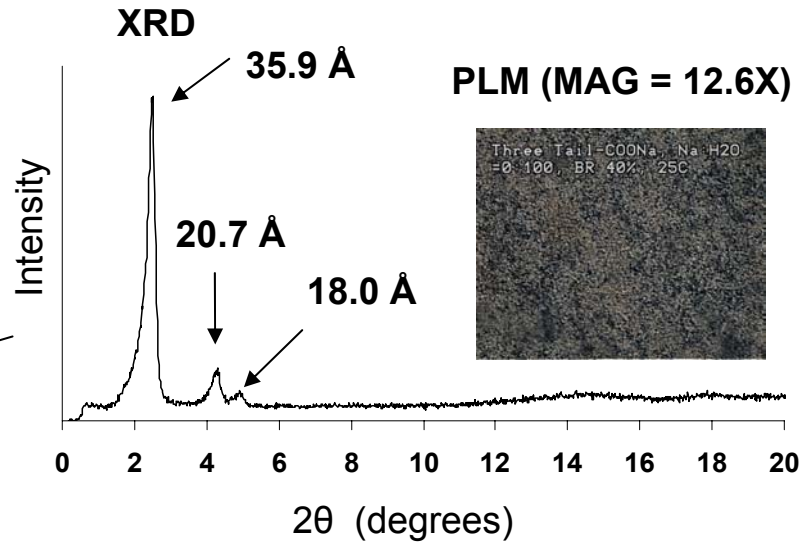
Blending Procedure and Structure Determination

- LLCs and H_2O were mixed and centrifuged three times (3800 RPM, 15 min.).
- Add the LLCs obtained in the above step with BR precursor solution (15 wt % in hexane) and then mix/centrifuge three times (3800 RPM, 15 min.).
- Phase structures of samples were determined by X-ray diffraction (XRD) and polarized light microscopy (PLM).

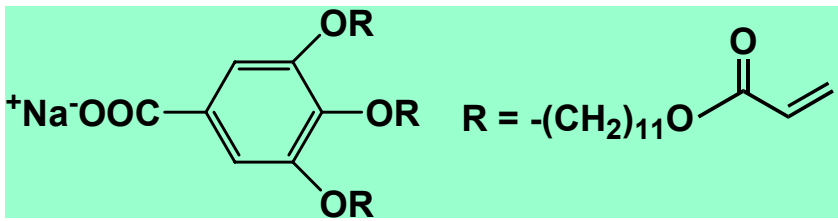
Phase Diagram of LLC-1 / BR System



T = 23 °C



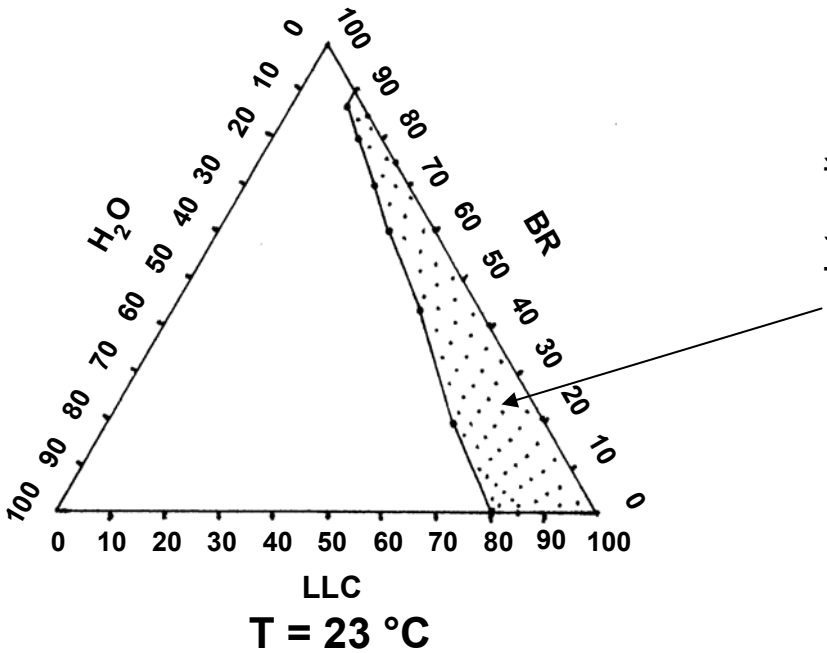
LLC: 60 %; BR: 40 %



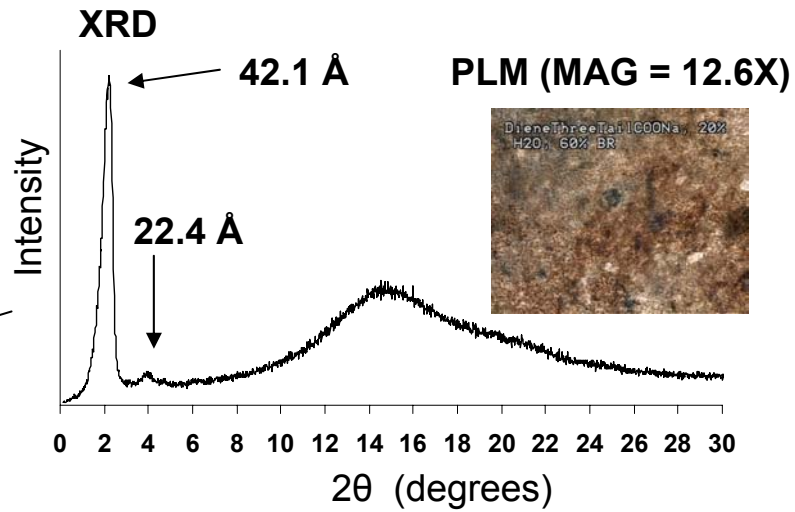
LLC - 1

- LLC-1 retains H_{II} phase even with BR content as high as 75 wt %.
- Retention of H_{II} structure upon photo-initiated radical polymerization.

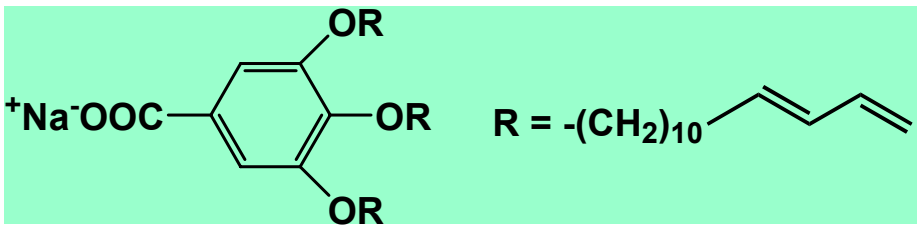
Phase Diagram of LLC-2 / BR system



T = 23 °C



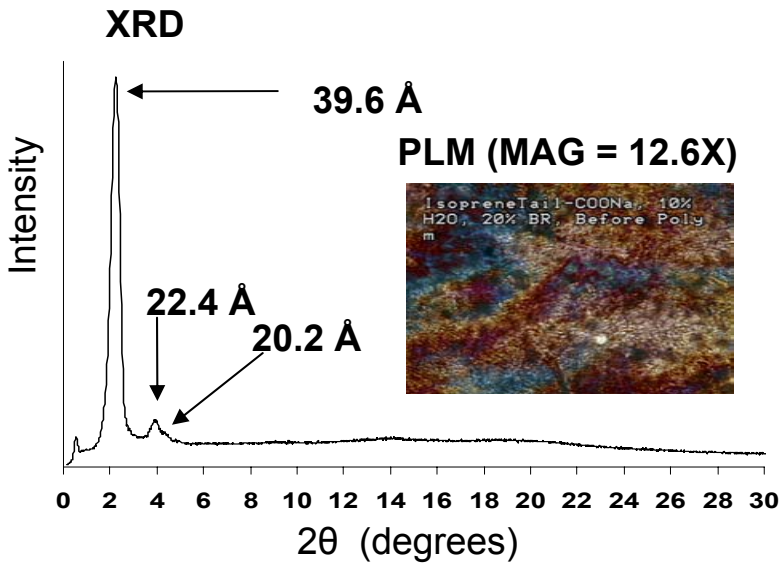
LLC: 32 %; BR: 60 %; H_2O: 8 %

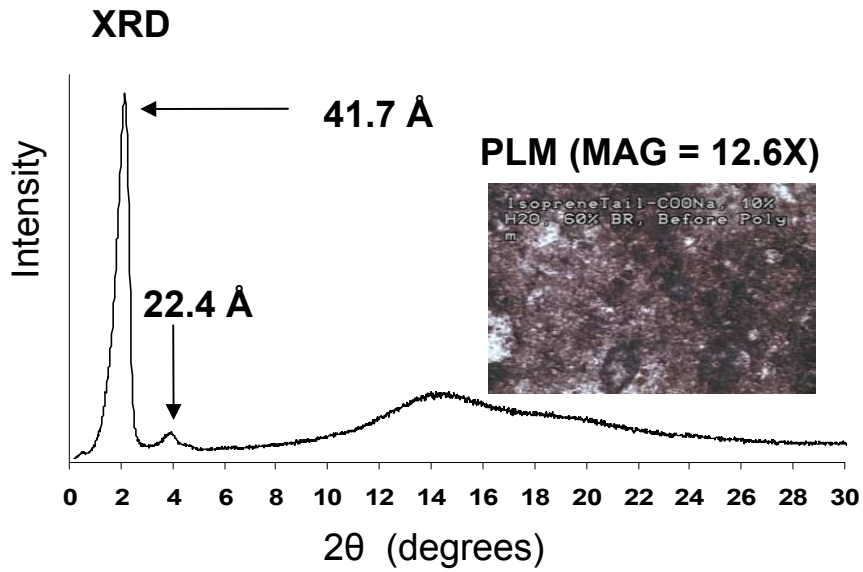


LLC - 2

- LLC-2 retains H_{II} phase even with BR content as high as 86 wt %.
- Retention of H_{II} structure upon photo-cross-linking.

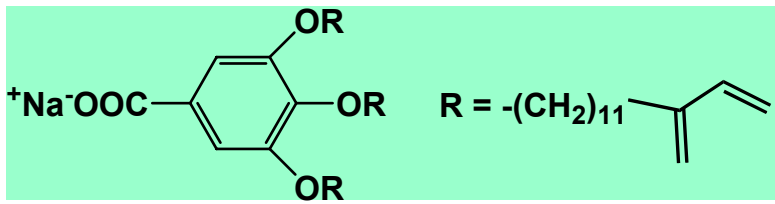
XRD Profiles of LLC-3 / BR System





LLC: 72 %; BR: 20 %; H_2O: 8 %

LLC: 36 %; BR: 60 %; H_2O: 4 %

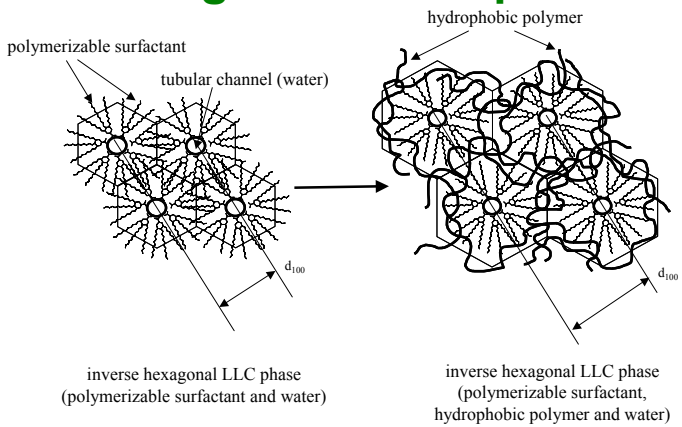


LLC - 3

- **LLC-3 retains H_{II} phase after mixing with up to 70 wt % BR.**
- **Retention of H_{II} structure upon photopolymerization.**

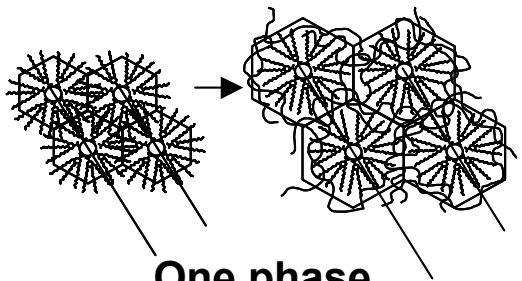
LLC / BR Microstructure Control: Swelling

Swelling of the LLC phase

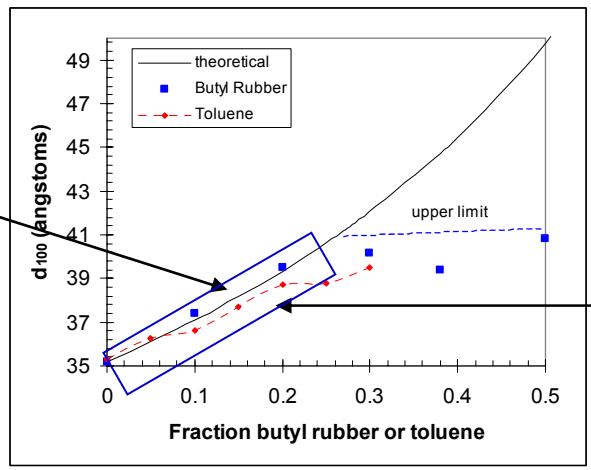


Experimental vs. theoretical swelling:

Both toluene and butyl rubber can swell the theoretical maximum up to about 25%

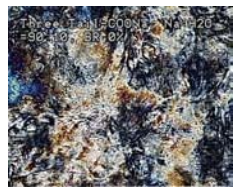


One phase LLC swelling

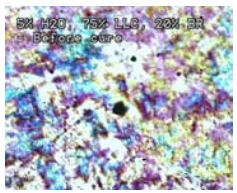


PLM (MAG = 12.6X)

Pure LLC



20 % BR

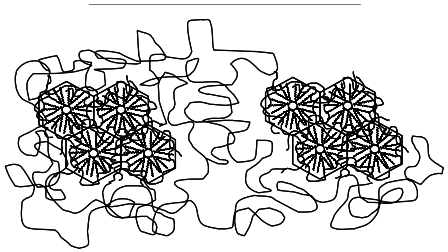


- **Unit cell of LLC phase increases with increasing BR content, up to 25 wt %.**

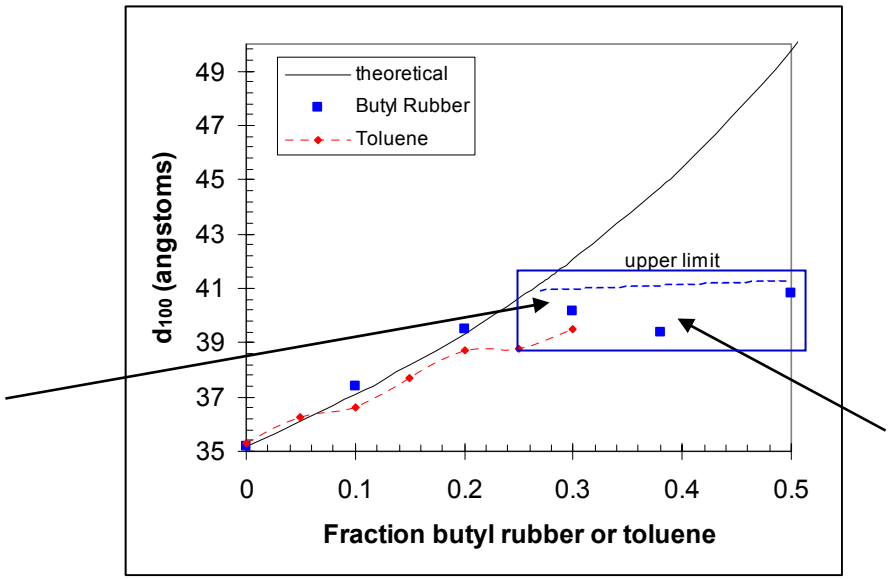
LLC / BR Microstructure Control: Phase Separation

Experimental vs. theoretical swelling:

Both toluene and butyl rubber can swell the theoretical maximum up to about 25%

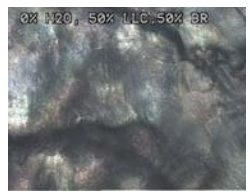


Two phase LLC swelling



PLM (MAG = 12.6X)

50 % BR



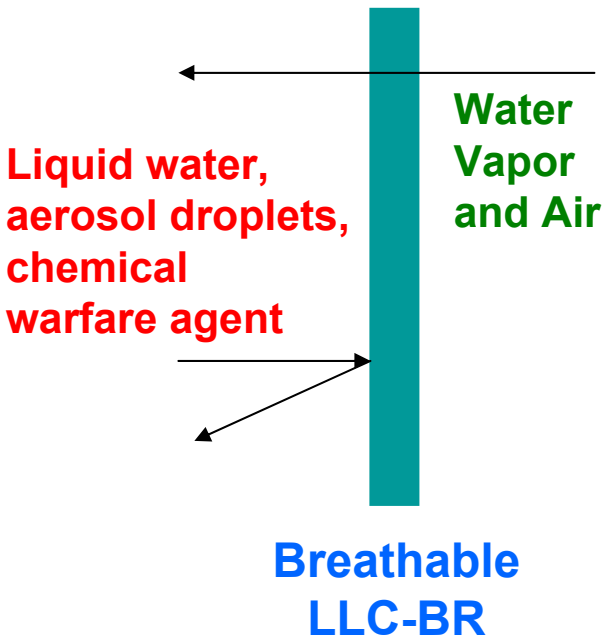
75 % BR

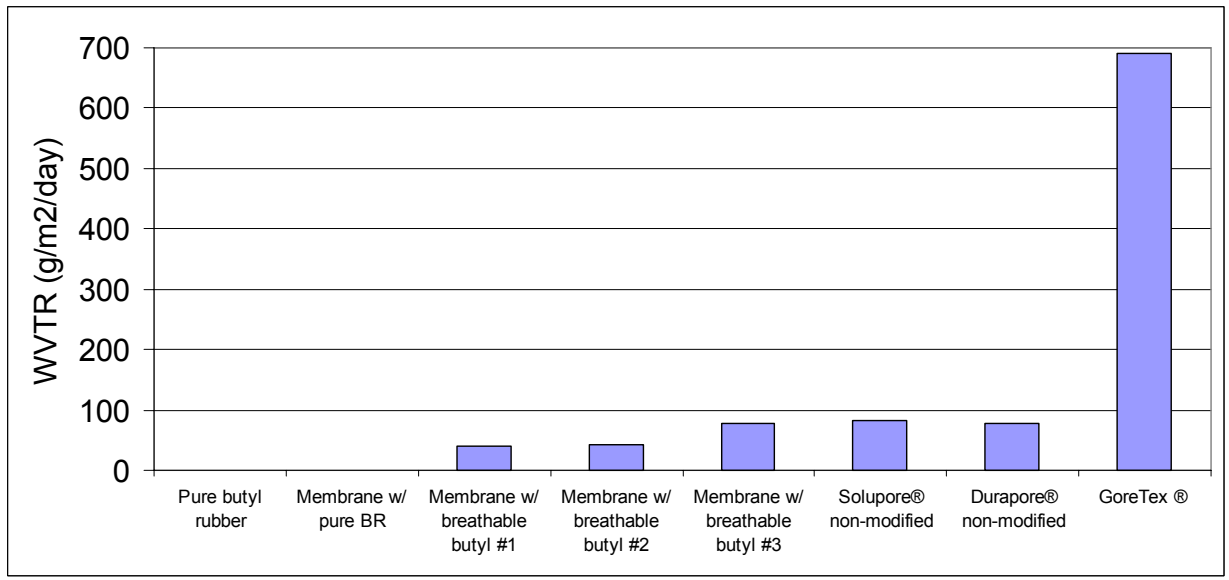
- **Above 25 wt % BR, BR chains go between LLC domains, and the phase separation occurs.**

Water Permeation Through LLC-BR Nanocomposites

Breathable BR membranes were produced using an ultraporous membrane support. The ultimate goal is to allow water vapor transport, while preventing chemical warfare agent (CWA) penetration.

- Water vapor transmission rate (WVTR) through membranes.
- 25 °C, 80% relative humidity to 0%.
- Mass transfer limited by ultraporous membrane support.
- Breathable BR composite membranes have 10% of the WVTR ("breathability") of GoreTex®

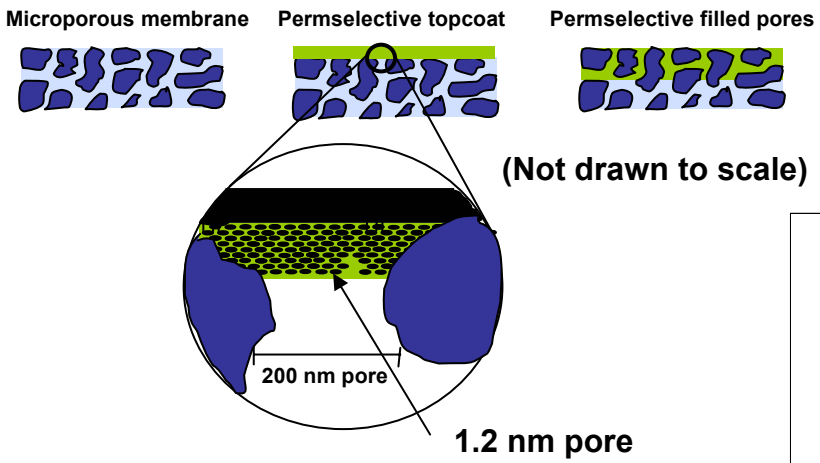


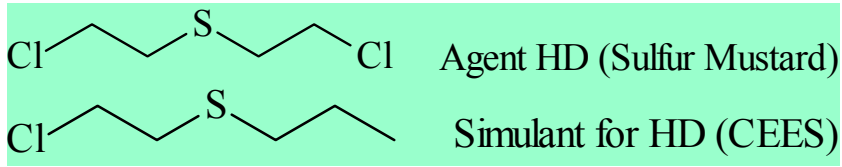


Note: GoreTex® has a higher reported WVTR for other testing conditions. The results above are for comparison purposes only.

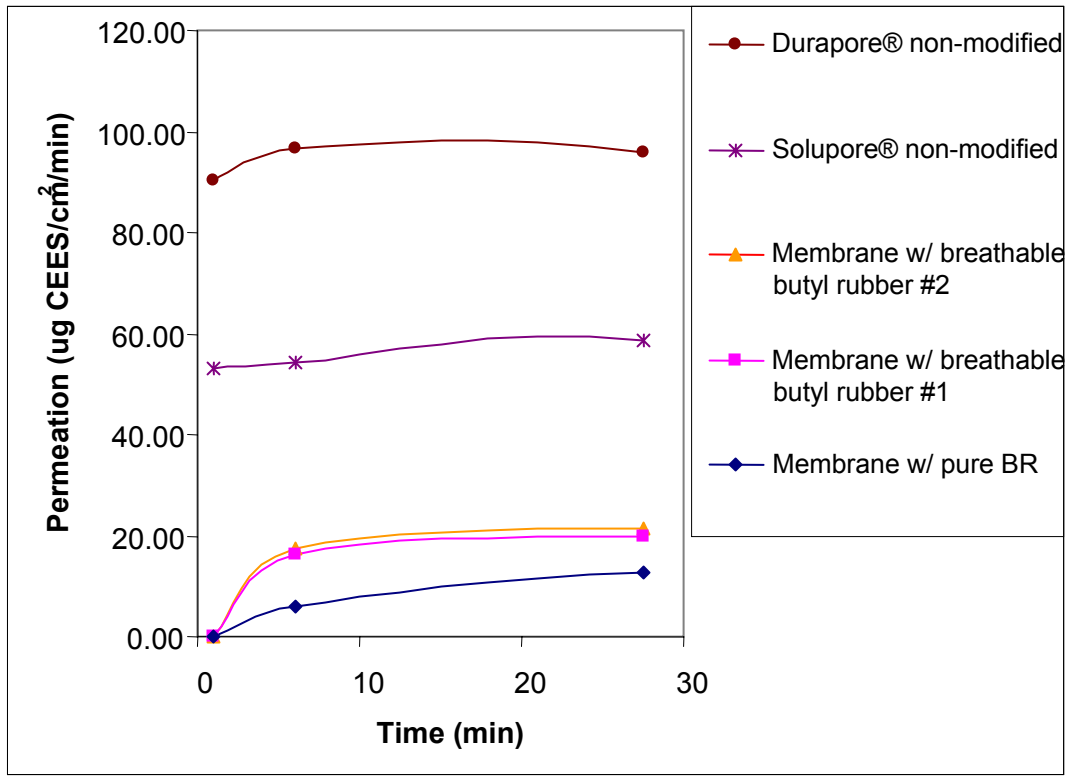
Chemical Warfare Agent Simulant Permeation Through Breathable LLC - BR Nanocomposites

Composite membranes





- Composite membranes were prepared with LLC / BR composites with varying amounts of BR.
- CEES permeation is compared for un-modified membrane supports and a composite membrane with either a breathable BR or a pure BR top-coat.
- Note that if the membranes were defect free, the pure BR should exhibit a higher resistance to CEES permeation than observed.
- Therefore, we expect even lower permeation for LLC / BR composites (breathable BR) with improved membrane production techniques.



Feed conditions: saturated CEES vapor, STP
Sweep conditions: N_2 and water vapor (25% rel. hum. At 25°C)

Summary and Future Work

Summary

- Nanoporous polymer composites were prepared by blending and copolymerizing LLC monomers with commercial BR polymer.
- The LLCs in the resulting polymer composites form the H_{II} phase and allow air and water vapor to permeate, but retard permeation of chemical agent simulants.

Future Work

- More detailed investigations on the vapor permeation of the LLC-BR composites are in progress.

Acknowledgments

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